Optical Materials 88 (2019) 128–133

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Self-assembly of colloidal Poly(St-MMA-AA) core/shell photonic crystals with tunable structural colors of the full visible spectrum

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ARTICLE INFO

Keywords:
Colloidal crystals
Photonic crystals
Polymer microspheres
Self-assembly
Structural colors

ABSTRACT

This study used the copolymer emulsion method to synthesize colloidal monodisperse core/shell microspheres composed of the poly(styrene-*co*-methyl methacrylate-*co*-acrylic acid) [Poly(St-MMA-AA)]. Colloidal photonic crystal (CPhC) films have prepared by using polymer composite microspheres and successfully fabricated via natural sedimentation. The synthesized results of polymer composite microsphere exhibited uniform and good morphology. The resultant of CPhC color films demonstrated vividly structural colors due to 3D CPhC nanostructures. The structural colors over full visible spectra could be tuned by controlling the filling factor of crystals and diameter of microspheres according to the Bragg law. Additionally, the structural color of Poly(St-MMA-AA) CPhC films has measured under the standard colorimetric system. This study demonstrated a approach to fabricate tunable structural color for numerous applications.

1. Introduction

Color has two major sources, namely, chemical pigments (or dyes) and photonic structures. Structural color is physical coloration due to the origin of photonic structures. In principle, structural color is a physical property effect to generate color through the scattering, refraction, interference, or diffraction of visible light by nanostructures with the scale of light wavelength in which the mechanism differs from chemical dyes and pigments. Compared with pigment color, structural color has more advantages, including nonfading property and environmental friendliness. These benefits lead to potential applications in various fields, including textile fabrics [1–3].

Structural color displayed by colloidal photonic crystals (CPhCs) has attracted increasing attention since its proposal [4–6]. The self-assembly strategy of CPhCs has been one of the most widely used methods because this strategy is relatively highly efficient, simple, and cost-efficient. The bright structural color is not easily influenced by the environment and not easily changes over time. The most important feature of CPhCs is the photonic band gap (PBG). The PBG position of CPhCs follows the Bragg's law, which can achieve the sensation of CPhCs by altering one parameter of CPhCs. In this study, we achieved the structural color of CPhCs change by altering the filling factor of crystals or the diameter of microspheres.

In recent years, the rapid development of polymer composite microspheres, made an important and critical role in many fields, including biomedical and biomedical disciplines, catalyst and coating production, information industry, polymer modification, microelectronics industry, nanotechnology, and column packing [7–10] due to the functional groups on their surface or inside part, which involve uniformly monodisperse microsphere size, large specific surface area, and a variety of functional groups. In addition, colloidal crystals from core-shell microspheres were obtained earlier and some of their optical properties have been investigated [11–13]. This study used hydrophobic monomer styrene (St), methyl methacrylate (MMA), and a hydrophilic monomer of acrylic acid (AA) as comonomers that are synthesized by emulsion polymerization to prepare nanometer level single monodispersion composite core/shell microspheres. Wang et al. have reported Poly(St-MMA-AA) core/shell microspheres with tough mechanical strength [8]. In the present study, Poly(St-MMA-AA) core/shell microspheres have prepared and measured, and structural color films were fabricated on glass petri dish through self-assembly of natural deposition. The polymer composite microspheres were distinguish using Fourier transform infrared (FT–IR) spectrum to research the formative factors of microspheres. The CPhCs were characterized using transmission electron microscope (TEM) and field emission scanning electron microscopy (FESEM) to prepare highly saturated and highly bright structural films.

The synthesized results of Poly(St-MMA-AA) microsphere exhibited uniform and good morphology. In addition, the resultant of CPhC films demonstrated vivid structural colors by 3D PhC nanostructure. The

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https://doi.org/10.1016/j.optmat.2018.11.020
Received 9 December 2017; Accepted 19 November 2018
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structural colors over the full visible spectra could be tuned by controlling the filling factor of crystals and diameter of microspheres according to the Bragg law. Furthermore, the structural color of Poly(St-MMA-AA) CPhCs was detected by using the standard Commission International d'Eclairage (CIE) 1931 colorimetric. We demonstrated the colloidal Poly(St-MMA-AA) core/shell PhCs that present tunable structural colors with a full color. This study demonstrated an inexpensive approach to fabricate tunable structural color for numerous applications.

2. Experimental section

2.1. Materials

Ammonium persulfate (APS; SHOWA) as initiator, sodium dodecylbenzenesulfonates (SDBS; TCI) as emulsifier, and ammonium bicarbonate (NH_4HCO_3; SHOWA) as buffer were directly used. St, MMA, and AA monomers were purchased from Acros Organics and were purified by reduced pressure distillation before used. Deionized (DI) water (PURELAB) was used for the entire experiments. Pure nitrogen (99.9999%) was used as received from the laboratory.

2.2. Synthesis of Poly(St-MMA-AA) core/shell microspheres

Colloidal polymer composite core/shell microspheres have synthesized according to literature reported emulsion polymerization [5,14], and the fabrication procedure was as follows. In this study, we changed the DI water content to tune the diameter of Poly(St-MMA-AA) microspheres. First, a three-necked flask was added the DI water, and equipped with nitrogen gas and placed in a water bath approximately 70 °C. Then, 800 mg NH_4HCO_3 and 100 mg SDBS were added into flask and stabled for 10 min. Subsequently, 1.0 g of AA, 1.0 g of MMA, and 30 g of St added into the mixtures under strong stirring for 1 h. Afterward, an aqueous solution (780 mg of APS dispersed in 20 g of DI water) added to the reaction solution approximately 70 °C. After strong stirring approximately 24 h, colloidal monodisperse core/shell microspheres composed of Poly(St-MMA-AA) were obtained. Finally, the varied content of DI water made the diameter of Poly(St-MMA-AA) microspheres become linearly dependent on the amount of DI water (Fig. 1). Poly(St-MMA-AA) microsphere sizes could be limited well from 170 nm to 240 nm by controlling the amount of DI water. With the increase of the amount of DI water, the size of Poly(St-MMA-AA) microsphere decreased. Afterward, polymer composite microsphere powders were used for further purification, collected through centrifugation at 24,652 relative centrifugal field (RCF, g). Samples with varying polymer composite microsphere sizes (diameter D_{sphere}) of 173 nm (Sample A), 211 nm (Sample B), and 240 nm (Sample C) were prepared (Table S1).

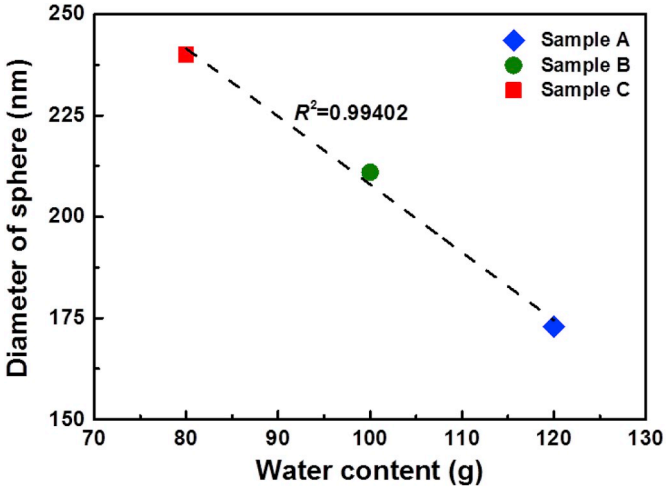

Fig. 1. Diameters of polymer composite microspheres dependent with the quantity of DI water, where black dashed line indicating linear fitting ($R^2 > 0.99$).

2.3. Preparation of Poly(St-MMA-AA) CPhC films

Colloidal monodisperse core/shell nanosphers composed of Poly(St-MMA-AA) have fabricated by emulsion polymerization, and then CPhCs were self-assembled by natural deposition on glass petri dish to obtain structural color films. Structural color fabrication on glass petri dish is illustrated in Fig. 2. The Poly(St-MMA-AA) CPhC films were prepared through natural deposition on glass petri dish [15,16]. Poly(St-MMA-AA) suspensions containing three kind of polymer microspheres with different diameter powder (Table S1) added in DI water approximately 10 wt percent (wt%) concentration were prepared by ultrasonic to complete dispersion. A glass petri dish was initially pre-treated with plasma to ensure it was hydrophilic. Then, Poly(St-MMA-AA) suspensions were dripped on the bottom of glass petri dish, covered, and placed in a general environment for 5 days without further sintering.

2.4. Characterization

The morphologies of colloidal monodisperse core/shell polymer microspheres were observed using TEM (JEOL). Meanwhile, the morphologies of CPhC films were observed using FESEM (Hitachi). FT–IR spectra (Frontier; PerkinElmer Inc.) within the range of 450–4000 cm^{-1} were measured using attenuated total reflection and recorded with a resolution of 1.0 cm^{-1}. A UV enhanced Xe lamp as a standard D65 white light source was used. The reflectance and color measurement of polymer composite microsphere films were determined using an HR2000 spectrometer (Ocean Optics). The color measurement of Poly(St-MMA-AA) CPhC films was calculated by SpectraSuite software (Ocean Optics) based on the standard CIE 1931 colorimetric system. Centrifugation (Heraeus multifuge X1; Thermo Scientific) was

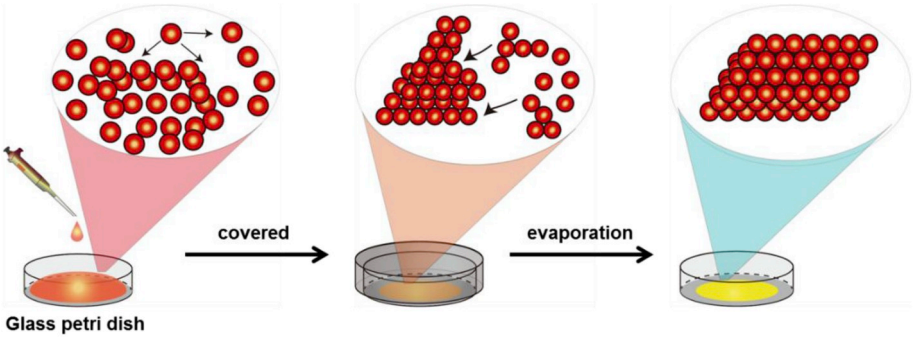

Fig. 2. Schematic showing the preparation of Poly(St-MMA-AA) CPhC color films through natural deposition. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

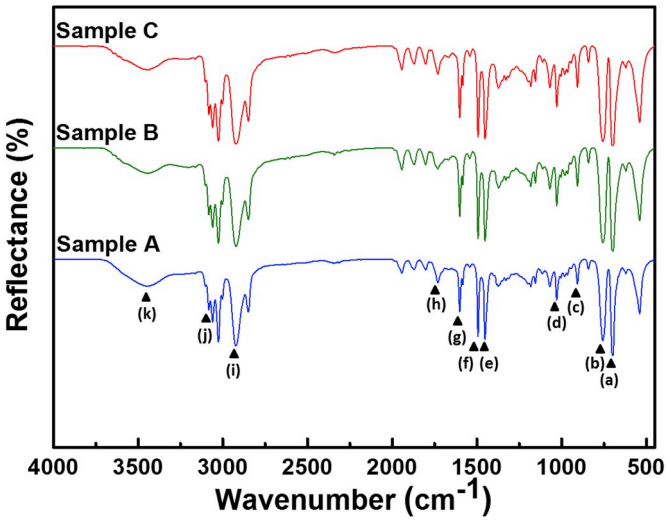

Fig. 3. FT–IR spectra of colloidal monodisperse core/shell polymer composite microspheres.

Table 1
Spectrum band assignment of colloidal monodisperse core/shell polymer composite microspheres.

Functional group	FT-IR peak position [cm^{-1}]
(a) C-H stretching	696
(b) C-H stretching	756
(c) C-O-C stretching	906
(d) C-O-C stretching	1028
(e) C-H stretching	1453
(f) C-H stretching	1494
(g) C-H stretching	1604
(h) C=O stretching	1730
(i) methylene carbon (-CH2)	2923
(j) methyl carbon (-CH3)	3086
(k) O-H stretching	3452

applied to purify Poly(St-MMA-AA) microspheres. Glass petri dishes with hydrophilic surface were treated with plasma (Zepto; Diener).

3. Results and discussion

3.1. FT–IR analysis of Poly(St-MMA-AA) core/shell microspheres

FT–IR spectra were used to characterize the synthesized Poly(St-MMA-AA) core/shell microspheres (Fig. 3) [17]. All samples were characterized using FT–IR to establish the chemical functional groups of the Poly(St-MMA-AA) core/shell microspheres. Table 1 lists the major characteristic peak positions of the functional groups in Poly(St-MMA-AA) core/shell microspheres. FT–IR spectra exhibited vibrational bands in the hydroxyl (O–H) of index (k) and the carbonyl (C=O) of index (h) stretching regions. The peak of index (c)–(d) was caused by the C–O–C stretching vibration, the stretching of C–H group of indexs (a)–(b) and (e)–(f), and the bands between index (i) and index (j), which are associated with the methylene carbon (CH_2 group) and methyl carbon (CH_3 group) vibrations, respectively. These results demonstrated the existence copolymer segments in the Poly(St-MMA-AA) microspheres.

3.2. TEM and FESEM analysis of Poly(St-MMA-AA) core/shell microspheres

Colloidal microspheres with uniform and good morphology of sphericity are important for CPhC materials. Therefore, Fig. 4 exhibited the TEM photographs of the colloidal monodisperse core/shell polymer composite microspheres. These polymer composite microspheres demonstrated a core/shell structure with spherical and monodisperse size. In addition, polystyrene is located on the core of the microspheres and a thin shell of Poly(MMA-AA) with carboxyl groups upon the surface of microspheres [8,18] as shown in Fig. 4. The results showed that good monodisperse Poly(St-MMA-AA) core/shell microspheres whose surfaces were smooth and clean could be obtained by emulsion polymerization.

In addition, FESEM was characterized the crystalline structure of polymer composite microspheres to form CPhCs. The CPhC color films with three kinds of microspheres with different D_{sphere} were grown through natural deposition [Fig. 5(a)–(c)]. Natural deposition enabled polymer composite microspheres to assemble with face-centered cubic (*fcc*) crystals, and top surfaces is the (111) crystallographic plane. We also observed that several cracks formed the non-closed-packed *fcc* crystals of Poly(St-MMA-AA) from low magnification of FE-SEM (Fig. S1). Therefore, the filling factor of microspheres (FF_{sphere}) in real CPhC films was lower than the theoretical value of *fcc* crystals (FF_{sphere} ~ 74%). These results caused the PBG of CPhCs red shifted.

3.3. Structural colors tuned by Poly(St-MMA-AA) microsphere diameter and filling factor

Fig. 6 exhibits the photographs of the CPhC color films composed of Poly(St-MMA-AA), and demonstrate bright and uniform structural colors. The visual appearance of Poly(St-MMA-AA) CPhC color films exhibiting vivid iridescent color was clearly changed by different diameters of Poly(St-MMA-AA) microspheres. Fig. 6 shows the three structural colors of blue, green, and red generated from the CPhCs and constructed by polymer composite microspheres with various diameters of 173, 211, and 240 nm. Therefore, structural colors vary with different microsphere sizes.

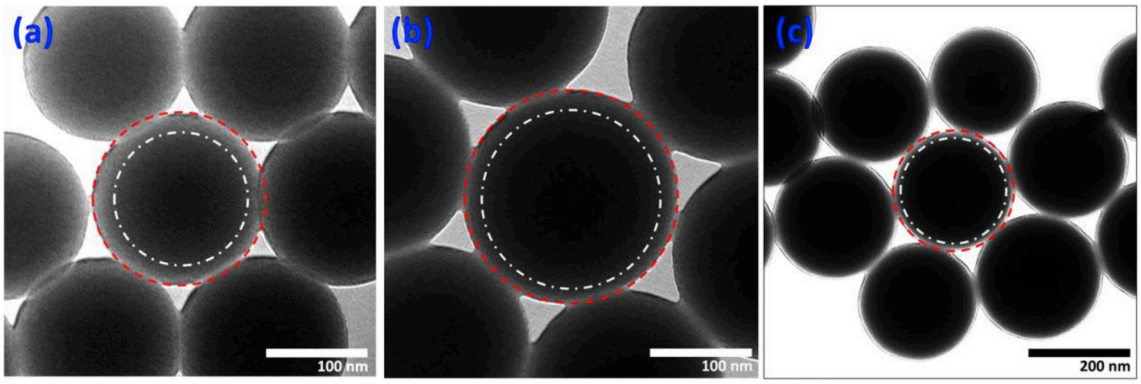

Fig. 4. High-magnification TEM photographes of Poly(St-MMA-AA) microspheres with core/shell of (a) 153/20 (Sample A), (b) 193/18 (Sample B), and (c) 222/18 nm (Sample C).

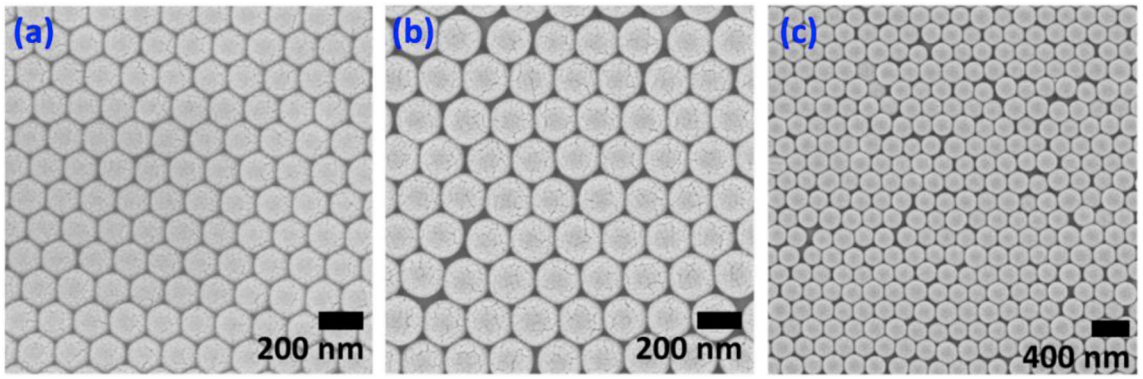

Fig. 5. FESEM photographs of Poly(St-MMA-AA) CPhCs with 10 wt% for (a) Sample A, (b) Sample B, and (c) Sample C.

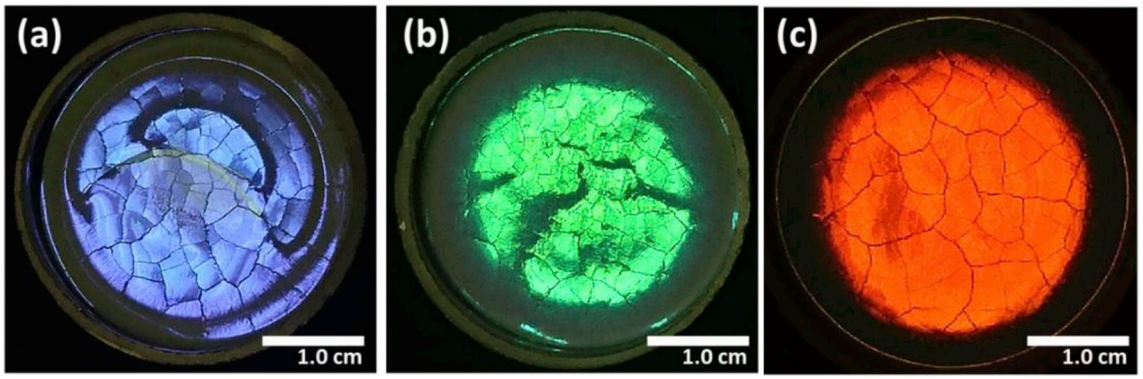

Fig. 6. (a) Sample A, (b) Sample B, and (c) Sample C of photographs of CPhC films composed of polymer composite microspheres prepared with varying diameters.

The reflectance spectra of three kinds of samples have measured by using UV–visible spectrometer. Fig. 7 exhibits the reflectance spectra of CPhCs with Poly(St-MMA-AA) microspheres, in which the D_{sphere} were 173 (Sample A), 211 (Sample B), and 240 nm (Sample C). Poly(St-MMA-AA) CPhCs exhibited reflectance positions at 420 (Sample A), 520 (Sample B), and 611 nm (Sample C), which corresponded to blue color, green color, and red color, respectively. The reflectance spectra of Poly (St-MMA-AA) CPhC color films with different D_{sphere} demonstrated different reflection wavelength positions. The analysis of color films showed that when the microsphere sizes increased form 172 nm–240 nm, the peak of reflectance spectrum moved to long-wave band and the structural color red-shifted, from 420 nm to 611 nm.

The theoretical and measured reflection wavelengths of the Poly(St-MMA-AA) CPhC color films can been determined based on the Bragg's and Snell's laws [Eq. (1)] [16,19], where λ_R is the reflection wavelength and α is incident angle of a 3D ordered crystal structure.

$$\lambda_R = \left[\frac{\pi}{3\sqrt{2}FF_{sphere}}\right]^{\frac{1}{3}}\left(\frac{8}{3}\right)^{\frac{1}{2}} D_{sphere}\sqrt{n_{eff}^2 - sin^2\alpha} \quad (1)$$

where D_{sphere} is the diameter of polymer composite microspheres, and n_{eff} is the effective refractive index of the CPhCs that was obtained using Eq. (2):

$$n_{eff}^2 = n_{sphere}^2 FF_{sphere} + n_{air}^2(1 - FF_{sphere}) \quad (2)$$

where $n_{sphere} = 1.5916$ is the refractive index of the polymer composite microspheres [20], and FF_{sphere} is the filling factor of the polymer composite microsphere.

For example, $D_{sphere} = 211$ nm and $FF_{sphere} = 0.74$ for theoretical *fcc* crystals of CPhCs in case sample B. Thus, $n_{eff} = 1.461$ can be obtained by Eq. (2). Therefore, the theoretical reflection peak position at normal incident ($\alpha = 0^{\circ}$) can be calculated by Eq. (1) to obtain 502 nm, which mismatches the measured normal reflection peak position $\lambda_R = 520$ nm, as shown in Fig. 7. In this study, natural deposition method produced various cracks and defects of Poly(St-MMA-AA) CPhC films that could cause the non-closed-packed CPhC films (Fig. S1), therefore that caused the red-shift of reflection peak [21]. Moreover, the theoretical value and experimental value of reflection peak position exhibited some differences. The discrepancy of the experimental value and the theoretical value has been previously reported [22] and suggested that deviation could be attributed to the shrinkage of the colloidal microspheres during drying, which resulted in non-closed-packed *fcc* crystal structures. The shrinkage of the colloidal microspheres could also be responsible for the appearance of the cracks. As a result, the difference between the experimental result and the theoretical result could be attributed to the presence of the cracks and defects in the colloidal crystals. Therefore, we can provide function f(FF_{sphere}) in terms of one dependent variable FF_{sphere} as Eq. (3):

$$\text{f}(FF_{sphere}) = \left[\frac{\pi}{3\sqrt{2}FF_{sphere}}\right]^{\frac{1}{3}}\left(\frac{8}{3}\right)^{\frac{1}{2}} D_{sphere} n_{eff} - \lambda_R \quad (3)$$

The solutions to f(FF_{sphere}) = 0 yields the solution to the "root" problem. Fig. S2 plots the function that can indicate one roots. We applied numerical bisection to have a solution for the root. Therefore, $FF_{sphere} = 0.517$ for Sample B case (Table S1) caused the reflection wavelength position to red-shift compared with those of the theoretical values.

The colors of Poly(St-MMA-AA) CPhC films have determined by the corresponding standard CIE 1931 colorimetric system. Color measurement was performed the Poly(St-MMA-AA) CPhCs under the standard D65 light source irradiating. CIE chromaticity coordinates of CPhC color films composed of polymer microspheres were determined by using SpectraSuite software [15,16]. The Poly(St-MMA-AA) CPhC color films was exhibited that the color coordinates of CIE (x, y) indicated the

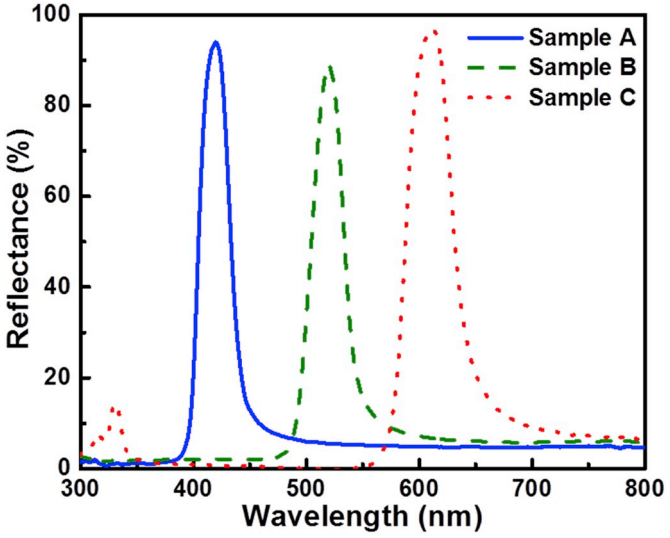

Fig. 7. Reflection spectra of Poly(St-MMA-AA) CPhC color films for Sample A (blue solid line), Sample B (green dashed line), and Sample C (red dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

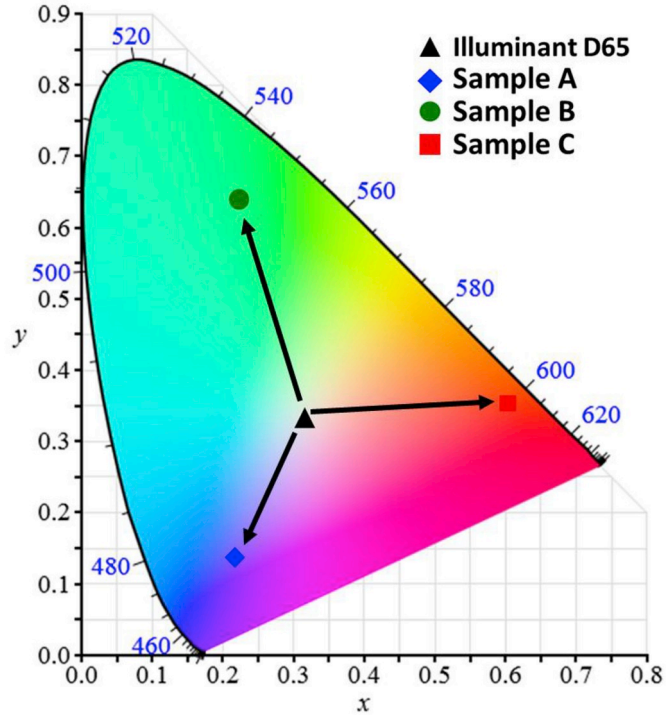

Fig. 8. CIE chromaticity diagram demonstrated the CPhCs composed of Poly(St-MMA-AA) for different samples with Sample A (diamond), Sample B (circle), and Sample C (square).

corresponding structural color in the CIE chromaticity diagram. For the D_{sphere} of 173 (Sample A, diamond), 211 (Sample B, circle), and 240 nm (Sample C, square), the structural colors were blue color, green color, and red color, respectively (Fig. 8). The three primary colors were achieved using the CPhC color films with Poly(St-MMA-AA) microspheres.

4. Conclusions

The structurally colored films of colloidal monodisperse core/shell microspheres composed of Poly(St-MMA-AA) have prepared through CPhCs. Poly(St-MMA-AA) CPhC structures have demonstrated tunable structural colors under natural lighting. The structurally colored films of colloidal Poly(St-MMA-AA) core/shell photonic crystals covered a full visible color from violet to red by tuning the filling factor of *fcc* crystals and diameter of polymer composite microspheres. Poly(St-MMA-AA) materials were systematically investigated by FT–IR spectrum. This study proposed approach offers tunable structural color for various applications.

Acknowledgments

This work is supported by the Ministry of Science and Technology (MOST), Taiwan, under contract numbers MOST 105-2221-E-035-041 and MOST 106-2221-E-035-076. The authors appreciate the Precision Instrument Support Center of Feng Chia University, Taiwan, that provided the measurement facilities. All author contributed equally to this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.optmat.2018.11.020.

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